Combining HC-SCR over Ag/Al$_2$O$_3$ and hydrogen generation over Rh/CeO$_2$-ZrO$_2$ using biofuels: An integrated system approach for real applications

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ABSTRACT

We report on a high NO$_x$ reduction activity over Ag/Al$_2$O$_3$ catalysts, using hydrogen produced in a fuel reformer. The focus of the study is to evaluate the performance of a hydrocarbon selective catalytic reduction (HC-SCR) catalyst in real conditions. Initially, the catalytic materials for the fuel reformer (Rh/CeO$_2$-ZrO$_2$) and the HC-SCR (Ag/Al$_2$O$_3$) were evaluated in separate bench-scale reactor setups. These two setups were subsequently joined into an integrated bench-scale reactor setup with the aim to evaluate the influence of the reformate on the HC-SCR activity in a controlled environment. In the final phase of the study a 4 wt.% Ag/Al$_2$O$_3$ catalyst doped with 100 ppm(w) Pt was scaled up and tested in a pilot-scale reactor setup. The pilot-scale reactor setup enabled evaluation of the HC-SCR activity in real exhaust gases generated by a single cylinder engine (genset) together with a hydrogen-rich gas supplied from a fuel reformer. Commercial biodiesel (NExBTL) was used as reducing agent for the HC-SCR as well as fuel in the fuel reformer for both the bench-scale and pilot-scale experiments. This study gives an excellent link between evaluations of the catalytic materials, controlled bench-scale experiments and applied engine experiments, proving a viable concept for lean NO$_x$ reduction together with onboard hydrogen production. A NO$_x$ conversion of above 70% was reached at temperatures below 250 °C, in bench-scale experiments when hydrogen produced in the fuel reformer is added.

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1. Introduction

Stringent emission legislations and limited fossil fuel resources are strong drivers for the development of more energy-efficient engine concepts. A durable system is the diesel engine, which uses high oxygen concentration in the combustion chamber, *i.e.* higher air-to-fuel (A/F) ratios compared to engine concepts based on stoichiometric combustion (spark ignition engines) [1]. The higher A/F ratio results in a more complete combustion, decreasing the fuel consumption and thus the emissions of anthropogenic CO$_2$. The increased A/F ratio also results in a lower exhaust gas temperature. The emission restrictions of today consider particulate matter (PM),

total hydrocarbons (THC), carbon monoxide (CO), non-methane hydrocarbons (NMHC) and nitrogen oxides (NO$_x$). Emissions of NO$_x$ are hazardous to the environment, acting as a source to ground level ozone, acid rain and eutrophication, as well as being directly harmful to humans [2,3]. The legislated maximum emission levels of NO$_x$ for heavy-duty vehicles have been reduced from 8.0 g/kWh in 1992 (Euro I), to 0.4 g/kWh in 2014 (Euro VI) [1], with even more stringent emission levels expected in the future. In addition legislation concerning restrictions in anthropogenic CO$_2$ is likely to come. The probable restrictions of anthropogenic CO$_2$, and the fact that the fossil fuel sources are dwindling, has resulted in the development of many types of biofuels and this trend is likely continuing. Solving the problem of NO$_x$ emission abatement, with biofuels as well as fossil fuels, is therefore of crucial importance.

The initial technique for reducing emissions were based on engine modifications, however as the restrictions became more stringent, engine modifications were no longer sufficient and new strategies for NO$_x$ abatement for the heavy-duty fleet were required. Today, the most well established strategy for decreasing

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NO_x emissions is selective catalytic reduction (SCR) using a water solution of urea (NH_2CONH_2) as reducing agent. Even though the method is well established, it is connected with significant drawbacks. One major drawback is the limited infrastructure for urea distribution [4]. Although urea is readily available in Europe, in the USA and in other industrialized parts of the world, large parts still lack access to urea solution [4]. There are also issues with reduced fuel capacity as a consequence of the extra urea tank needed and the risk of ammonia slip [4]. One drawback connected to the method itself is the risk of deposition of byproducts and urea compounds, *e.g.* formation of biuret, cyanuric acid, ammelide *etc.*, in the exhaust after-treatment module [5–7]. In addition, the effect on fuel penalty from the addition of urea is not negligible. Approximately 2 g of urea solution is required for every 1 g of reduced NO_x. As the price of urea solution is approximately half of that of diesel in Europe, the resulting fuel penalty is approximately 0.5%. However, this only takes into account the financial aspects of fuel penalty and not the added CO_2 from the production and distribution of urea solution.

One possible technique circumventing these problems is selective catalytic reduction of NO_x using hydrocarbons, *i.e.* fuel or derivatives from the fuel, HC-SCR [8]. Advantages for the HC-SCR system is therefore many as inherently all chemical and mechanical issues concerning urea are avoided. Further, as the fuel is used as reducing agent, no additional components are needed and the system can be utilized for vehicles worldwide. Silver-alumina (Ag/Al_2O_3) has been pointed out as a potential catalyst for HC-SCR, displaying promising results for a variety of hydrocarbons, including fossil fuels and biofuels [9,10]. The main drawback with the Ag/Al_2O_3 system was long that the system required relatively high temperatures to reach high activity. Nevertheless, the active temperature window for HC-SCR over Ag/Al_2O_3 may be shifted towards lower temperatures, provided a small amount of hydrogen is introduced to the exhaust gas, as showed by Satokawa in 2000 [11]. The addition of hydrogen further results in an over-all increase in the NO_x reduction, where the highest activity generally has been reported over Ag/Al_2O_3 catalysts containing 2 wt.% Ag [12,13]. It has also been shown that doping a Ag/Al_2O_3 catalyst with trace amounts of platinum can increase the low temperature activity [14].

The remaining major issues with HC-SCR are the increased fuel penalty, the NO_x reduction activity at low temperatures, and the hydrogen supply to the catalyst. There are several options for both storing and producing hydrogen onboard vehicles [15]. Today the hydrogen vehicles often have a tank where hydrogen is stored either compressed or cooled. The main drawback with this option is the need for hydrogen fuel stations and infrastructure, which is very limited today. A more universal option would be on-board production of hydrogen with the propellant as fuel. This can either be done by exhaust gas recirculation (EGR) reforming, with addition of extra diesel to the EGR flow, to supply the HC-SCR with sufficient hydrogen [16,17], or in a separate fuel reformer where additional applications which utilizes hydrogen, are possible. Such applications are *e.g.* (i) as fuel in a fuel cell auxiliary power unit (FC APU) generating electricity, (ii) initial heating of the after-treatment system, (iii) additive to enhance the combustion and (iv) regeneration of NO_x trap catalysts. Out of these applications FC APU has the greatest prospect of reducing the overall emissions by producing the required electricity for cabin comfort during idling. Another benefit with adding hydrogen, besides the increased NO_x reduction activity, is that the activity is less sensitive for variations in the gas hourly space velocity (GHSV), *i.e.* the exhaust gas flow [18].

As stated previously, the fuel penalty is one of the major problems with the HC-SCR system. The fuel penalty for the HC-SCR derives from both the increase in consumed diesel in the form of reducing agent and from the use of diesel in the fuel reforming to hydrogen. Activities over 95% in the range between 225 and

450 °C have been reported, using 7200 ppm H_2 [13]. In general, increasing the HC/NO_x ratio also leads to higher NO_x reduction efficiencies, however synthetic gas bench experiments have indicated that HC/NO_x ratio of 6 is sufficient for a high NO_x conversion [19]. With the legislative demands of 0.1 g NO_x/kWh tail pipe out, this would result in a fuel penalty of about 1.8 gram of diesel per gram of NO_x removed from the exhaust gases when using a low NO_x emitting engine (1.0 g NO_x/kWh engine-out). In addition, approximately 2 g diesel/kWh for H_2 production (1000 ppm in the exhaust gas flow) would be needed. This would result in a fuel penalty of about 2.3% [20].

The influence of hydrogen on the HC-SCR reaction over Ag/Al_2O_3 has been studied extensively since it was first reported in 2000 [11]. These experiments have mostly focused on the actual reaction mechanism behind and the catalytic properties of the Ag/Al_2O_3 catalyst [21–24]. To better isolate the effects that the reformate and the engine exhaust gases have on the performance of the HC-SCR catalyst, these systems need to be studied together.

To the authors' knowledge there have been limited studies where the hydrogen production step has been included when evaluating HC-SCR and even fewer where real engine exhausts together with hydrogen production and real fuel as reducing agent are used. Zhao et al. [25] studied the combination of fixed-bed fuel reformer for n-octane over a nickel-based catalyst in combination with a HC-SCR catalyst in synthetic exhaust gases. In addition, experiments with similar setup as the one used in the pilot-scale reactor setup have been performed [17,26,27]. The experiments showed a significant enhancement of the NO_x conversion at low-temperatures (130–330 °C), owing to hydrogen addition in real exhaust conditions. In the present study however, in-house synthesized catalysts for fuel reforming and HC-SCR were evaluated in a controlled environment, using both separate bench-scale reactor (BSR) setups and an integrated BSR setup. Subsequently, a pilot-scale reactor setup (PSR) with a single cylinder genset engine was used, with a scaled up HC-SCR catalyst. As the new emission abatement techniques need to comply with the increasing amount of biofuels, this study was performed using a commercial biodiesel (NExBTL, Neste Oil), both as the reducing agent for the HC-SCR catalyst and as the hydrogen source for the reformer catalyst. The study investigates both bottled hydrogen and hydrogen derived from a separate fuel reformer, while integrating HC-SCR and fuel reforming.

This study aims to illustrate the effects of completely integrating the HC-SCR and fuel reforming systems, ranging from BSR experiments, with simulated exhaust gases, to PSR experiments using real engine exhaust gases. As a result, the study gives an excellent link between laboratory results and applied engine results, showing a viable concept for onboard hydrogen production. In addition, the fuel used as reducing agent for the HC-SCR and as hydrogen source in the fuel reformer was the biodiesel NExBTL.

2. Experimental methods

As the main goal of this work is to illustrate the effects of integrating the HC-SCR system with a fuel reforming system, great focus has been paid to the experimental setup. The catalysts chosen for the study have been thoroughly evaluated in previous papers [14,28]. In the first part of the study, an integrated bench-scale reactor setup (BSR) was constructed by combining the flow reactor in Ref. [29] with the fuel reformer in Ref. [28], in order to evaluate the integrated systems under controlled conditions. To evaluate the combined system further, a pilot-scale reactor (PSR) setup was constructed. This system was tailored for up-scaled integration experiments and utilizes a genset engine (Yanmar, L100) to generate exhaust gases with a composition close to that of a heavy-duty vehicle.

2.1. Catalyst preparation

2.1.1. HC-SCR catalyst

Ag/Al_2O_3 samples were prepared by a sol-gel based method including freeze-drying [29], with a nominal silver loading of 2 and 4 wt.%, respectively. In addition, the 4 wt.% sample was also prepared with addition of 100 ppm(w) platinum. The catalysts are denoted as; 2 wt.% silver on alumina: Ag2, 4 wt.% silver on alumina: Ag4 and 4 wt.% silver on alumina with 100 ppm(w) platinum by weight: Ag4Pt100. The alumina precursor (aluminum isopropoxide, >98%, Aldrich) was added to milli-Q water and heated to 82 °C during vigorous stirring. Subsequently, the silver precursor ($AgNO_3$, >99%, Sigma–Aldrich), and for the Pt doped sample a platinum precursor ($Pt(NO_3)_2$ solution type K, Heraeus), was added. The pH was adjusted to 4.5 by addition of HNO_3 (10%, Fluka), resulting in the formation of a sol. The sol was stirred for 12 h, after which a major part of the solvent was removed using a heated vacuum system. The resulting gel was freeze-dried in order to preserve the microporous structure of the aluminum oxy-hydroxide (AlOOH) and to minimize the migration of silver in the pores during the drying process. The resulting cryogels were calcined in air at 600 °C for 6 h (phase transformation of AlOOH to γ-Al_2O_3) and finally ground to a fine powder.

The resulting catalyst powder was then wash-coated onto cordierite monoliths (Corning Celcor®, 400 cpsi), 20 by 20 mm for the BSR [29] and 90 by 95 mm for the PSR. The corresponding loading on the monoliths are; 2 wt.% Ag ∼ 36 g/ft^3, 4 wt.% Ag ∼ 72 g/ft^3 and 100 ppm(w) Pt ∼ 0.2 g/ft^3. A wash-coat slurry was prepared with 20 wt.% (bench-scale) or 15 wt. % (pilot-scale) dry content, where the dry part consisted of 20 wt.% AlOOH-binder (Disperal P2, Sasol) and 80 wt.% catalyst powder. The solvent consisted of 50 wt.% H_2O and 50 wt.% ethanol for the bench-scale monoliths, and 67 wt.% H_2O and 33 wt.% ethanol for the pilot-scale monoliths. Additional solvent and HNO_3 were added in order to control the viscosity and pressurized air was used to remove excess slurry in the monolith channels. The monoliths were submerged in the slurry, dried at 90 °C and then subjected to a fast calcination at 600 °C in air for 2–5 min. The wash-coating procedure was repeated until sufficient amount of wash-coat (20 wt.% of the final weight) had been deposited, where after the coated monolith samples were calcined in air (600 °C, 3 h). The pilot scale monoliths were subsequently canned prior to installing in the PSR.

2.1.2. Reforming catalyst

The catalytic material used in the fuel reformer was 3 wt.% Rh supported on high surface area CeO_2-ZrO_2 (MEL Chemicals, 16.5% CeO_2/ZrO_2) prepared by the incipient wetness impregnation method. As metal precursor, Rh nitrate solution was used ($Rh(NO_3)_3$ solution, 9.53, w/w, Sigma–Aldrich). The Rh nitrate solution was diluted in water to a volume corresponding to approximately twice the pore volume of the support material used. The Rh solution was then carefully added drop-wise to the support until the saturation point was reached. When the saturation point was reached the powder was dried in air at 110 °C for 3 h. This was repeated until all the Rh solution was impregnated on the powder. Subsequently, the catalytic material was calcined in air at 800 °C for 3 h. The calcined catalytic powder was then suspended in ethanol, (approximately 16 wt.% dry weight) and ball milled for a minimum of 24 h. The structural support used was honeycomb cordierite monoliths (Corning Celcor®, 400 cpsi, l = 30 mm, Ø = 20 mm) on which the catalyst powder was applied by dip coating. The monoliths were dipped in the slurry until the catalyst loading was approximately 20 wt.%, corresponding to a loading on the monoliths of ∼90 g Rh/ft^3. Between each dip, the monoliths were carefully dried in pressurized air and then dried in air at 110 °C

Table 1
Characteristics of the fuels used during the experiments.

Properties	NExBTL [33]	VSD10[c]	Unit
Sulfur content	<1	<3	ppm(w)
Min. boiling point	180	–	°C
Dist. 95% evap.	293	346	°C
Aromatics[a]	<0.31	3.8	wt.%
Carbon/hydrogen ratio	5.6	6.4	wt./wt.
P, K, Ca, Na, Mn[b]	<1	n/a	ppm

[a] Includes mono-, di-, and tri+-aromatics.
[b] Potential catalyst poisons.
[c] Volvo Standard Diesel.

for 45 min. After the coating, the monoliths were calcined again in air at 800 °C for 3 h.

2.2. Bench-scale reactor setup

In order to evaluate the HC-SCR catalyst in combination with hydrogen supplied by a fuel reformer, an integrated bench-scale reactor setup was built. The BSR setup consisted of a HC-SCR reactor and a fuel reforming reactor. Each reactor configuration has been evaluated thoroughly earlier for various catalytic materials [28,29]. All the HC-SCR catalysts described in Section 2.1 were evaluated (Ag2, Ag4 and Ag4Pt100). These catalysts have previously been evaluated thoroughly with bottled hydrogen [14]. The catalytic material used in the fuel reformer was 3 wt.% Rh supported on high surface area CeO_2-ZrO_2. Prior to the experiments in the integrated rector setups, the fuel reforming catalyst was evaluated for stability and durability in a separate experiment. The commercial biodiesel, NExBTL was used both as fuel in the fuel reformer and as reducing agent in the HC-SCR reactor. The physical and chemical properties of the fuel can be found in Table 1. The integrated BSR setup was built according to the schematic overview in Fig. 1.

The HC-SCR reactor consisted of a horizontally mounted quartz tube (Ø$_{inner}$ = 22 mm, l = 600 mm) heated by high temperature heating tape. The monolith sample was placed close to the outlet, maximizing the gas heating. The temperature was measured using type K thermocouples and controlled by PID controllers. The inlet gas flow composition (200 ppm NO, 10 vol.% O_2 from air and $N_{2,balance}$) was regulated by three separate mass flow controllers (Bronkhorst Hi-Tec). The hydrocarbon reductant was vaporized using a controlled evaporator mixer system (CEM, Bronkhorst Hi-Tec). Steam equal to an inlet concentration of 5 vol.% was generated by saturating N_2 in water at elevated temperature. The total inlet gas flow was 3500 cm^3/min, corresponding to a gas hourly space velocity (GHSV) of 33,200 h^{-1}. The exhaust gases were analyzed by an FTIR gas-analyzer (MKS^{TM} 2030 HS).

To produce the reformate a fuel reformer was used. The reactor consisted of a horizontally mounted high temperature steel reactor (Sandvik 253 MA, Ø$_{inner}$ = 24.3 mm) with external heating. To avoid bypassing, the monolith is wrapped in ceramic tape prior to mounting it in the reactor. The temperature was measured before and after the monolith. The gas flows (synthetic air and N_2) were regulated by two separate mass flow controllers (Bronkhorst®, El-Flow), the liquid fuel flow was regulated by a Coriolis mass flow controller (Bronkhorst®, Mini Cori-Flow) and the deionized water with a continuously operating syringe pump (WPI, Aladdin). The N_2 and synthetic air were mixed and heated prior to the introduction of water. The water was evaporated and mixed with the hot gases in a static mixer (SMX DN4, Sulzer). The gas mixture flow then enters the fuel vaporization chamber, into which the fuel is sprayed, by an N_2-assisted high-pressure nozzle, facilitating a smooth evaporation of the fuel. The concentration of hydrogen in the dry reformate was measured continuously with a mass spectrometer (V & F Instruments Inc., H-sense). Dry reformate was used
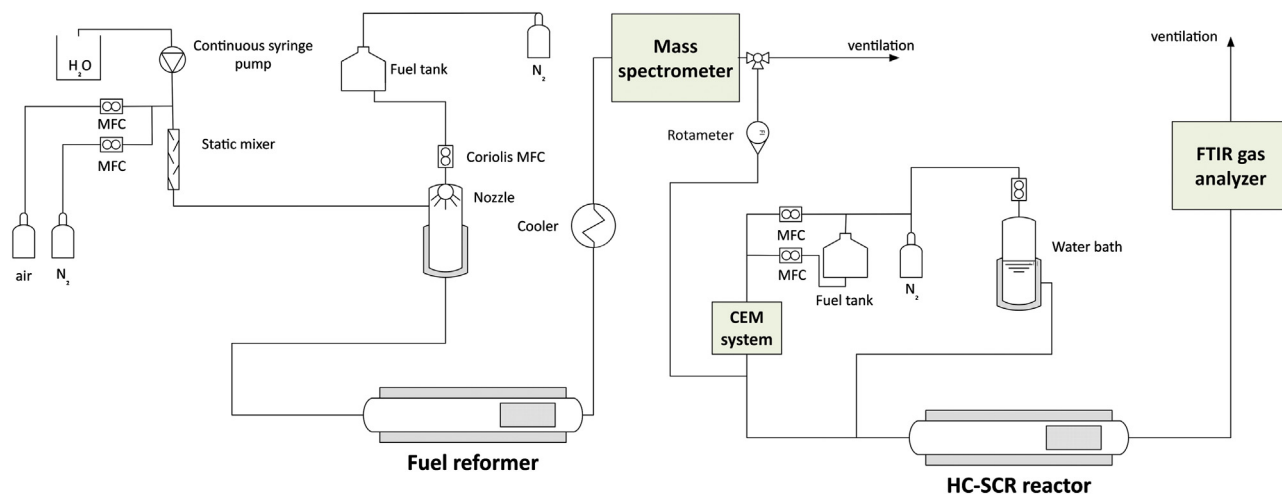
Fig. 1. Schematic sketch of the bench-scale reactor setup with separate HC-SCR reactor and fuel reformer. Inlet composition to the HC-SCR was 10 vol.% O_2, 5 vol.% H_2O and C/N = 6. The process parameters in the fuel reformer were H_2O/C ~2.5, O_2/C ~0.45, 750 °C and GHSV ~20,000 h^{-1}. The fuel used (both as reducing agent in HC-SCR and as fuel in the fuel reformer) was commercial biodiesel (NExBTL). The gas and liquid flows were regulated by means of mass flow controllers (MFC).

as hydrogen source to the HC-SCR reactor. To achieve the correct concentration of hydrogen in the feed to the HC-SCR catalyst, the volumetric flow of reformate was measured by a rotameter and regulated with a needle valve.

Prior to the integration experiments, the HC-SCR catalyst was conditioned at 550 °C in 10 vol.% oxygen in nitrogen. The NO_x reduction was investigated at steady-state conditions between 225 °C and 400 °C in 25 °C steps. The C/N molar ratio was kept constant at 6 during all experiments, corresponding to a C_1-concentration of 1200 ppm. Likewise, the aging characteristics of the fuel reformer catalyst were thoroughly investigated. This was performed in the bench-scale fuel reformer setup described in detail previously [28] using NExBTL as fuel. Prior to the aging experiments the reforming catalyst was treated in N_2 at 950 °C for 30 min and then aged for approximately 65 h. The aging consisted of several sequential temperature ramps from 650 °C to 950 in 50 °C steps with steady state measurements of approximately 40 min at each temperature. Between each temperature ramp the catalyst was regenerated in a mixture of O_2/N_2/steam at elevated temperature. The process parameters were H_2O/C ~2.5, O_2/C ~0.45 and GHSV ~50,000 h^{-1}. For the last temperature ramp (~65 h on stream) the GHSV was decreased to ~20,000 h^{-1} in order to mimic the reformate composition in the BSR and PSR experiments. Normally, reforming for automotive applications is performed at GHSV at 10,000–20,000 h^{-1}. However, this methodology limits the possibility to study the aging patterns due to the proximity of total fuel conversion.

Formation of nitrogen containing species, other than NO and NO_2, *i.e.* NH_3, HNCO, N_2O and cyanide species, were monitored. The concentrations of HNCO and N_2O were negligible («5 ppm) and therefore excluded from the NO_x reduction calculations. However, the concentration of NH_3 was significant and was therefore included in the NO_x reduction calculations. The NO_x reduction was derived from Eqs. (1) and (2).

$$NO_x = NO + NO_2 \tag{1}$$

$$NO_{x,\text{reduction}}(\%) = \frac{NO_{x,in} - NO_{x,out} - NH_{3,out}}{NO_{x,in}} \tag{2}$$

2.3. Pilot-scale reactor setup

The pilot-scale reactor experiments were performed at Advanced Technology and Research, Dep. of Energy Efficiency and Environment, Volvo Group Trucks Technology, Sweden. In the PSR experiments the 4 wt.% silver on alumina with 100 ppm(w) platinum (Ag4Pt100) HC-SCR catalyst was evaluated in real exhaust gases together with hydrogen supplied from a fuel reformer, and from a gas bottle, and NExBTL was used as reducing agent as well as fuel in the fuel reformer.

The exhaust gases were generated by a genset (DX 6000 TE XL C, Yanmar) propelled by VSD10 diesel. The genset generated an exhaust gas flow of ~450 dm^3/min containing ~420 ppm NO_x, depending on the operation mode. The exhaust gases were initially led through a diesel oxidation catalyst (DOC) (l = 150 mm, Ø = 140 mm) with a separate diesel injection. The DOC was used to regulate the heat of the exhaust gases and the operating temperature for the HC-SCR catalyst. The exhaust gas then passed through a diesel particulate filter (DPF), removing the particulates, and subsequently to the Ag/Al_2O_3 HC-SCR catalyst. The Ag/Al_2O_3 catalyst consisted of two sequential monoliths (l = 95 mm, Ø = 90 mm, V_{tot} = 1.2 dm^3), resulting in an approximate GHSV of 22,300 h^{-1}. Prior to the HC-SCR catalyst an air-assisted diesel injection system and a hydrogen injection nozzle were mounted. The hydrogen could be fed either from a gas bottle or from the fuel reformer. The gas composition was measured with an FTIR gas analyzer equipped with a sampling pump (MKS^{TM} 2030 HS). The gas composition could be monitored either upstream or downstream of the HC-SCR catalyst. The temperature of the exhaust gases was measured before the HC-SCR catalyst. An overview of the system used in the PSR experiments can be seen in Fig. 2. The physical and chemical properties of the fuels used during the experiments are given in Table 1.

The fuel reformer consisted of a vertically mounted stainless steel reactor with external heating. To avoid bypassing around the monolith, it was wrapped in ceramic tape prior to mounting it in the reactor. The size of the monolith was 9.4 cm^3 (l = 30 mm, Ø = 20 mm). The gases (N_2 and synthetic air) and fuel were regulated by three separate mass flow controllers (MFC) (Brooks Instruments). The water was pumped with a continuous syringe pump. The water and fuel was introduced and vaporized prior to the reactor. In front of the monolith a quartz plate was mounted to enhance the mixing of the reactants and ensure complete evaporation of the liquid reactants. The reformate could either be used as hydrogen source for the HC-SCR or be analyzed by an IR gas-analyzer (Sick Maihak). The analyzed concentrations were CO, CO_2, CH_4, O_2 and H_2 based on dry reformate. The GHSV was approximately 20,000 h^{-1}, H_2O/C = 3.8 and O_2/C = 0.4. The fuel reformer was operating at two
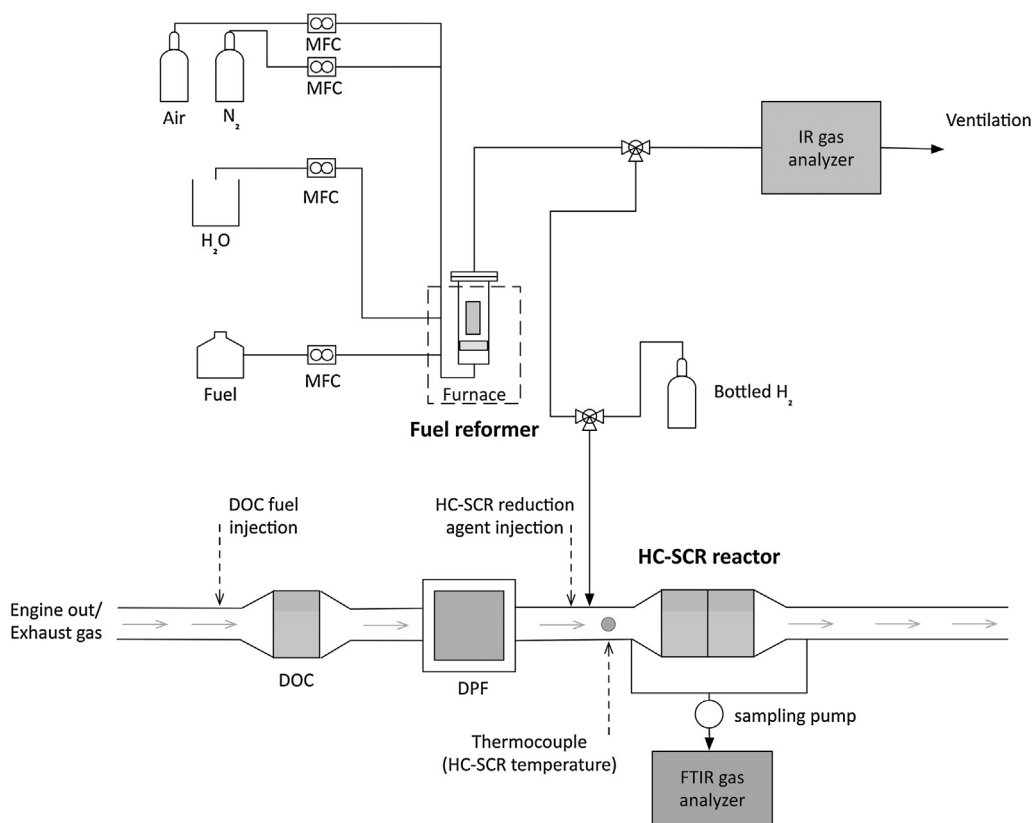
Fig. 2. Schematic sketch of the pilot-scale setup used for evaluating the HC-SCR catalyst together with real exhaust gases produced from a genset engine. The hydrogen could either be introduced from the separate fuel reformer or directly from a gas bottle. The fuel used in the fuel reformer as well as reducing agent was the commercial biodiesel, NExBTL. The gas and liquid flows to the fuel reformer were controlled by mass flow controllers (MFC). Prior to the HC-SCR catalyst, a diesel particulate filter (DPF) was mounted to remove the particulates from the engine. To enable heating of the exhaust gases, a diesel oxidation catalyst (DOC) with separate HC dosing was used.

different operating points, referred to as the low and high point, depending on the H_2 concentration in the exhaust gas feed. The low point was set to deliver a reformate flow corresponding to $\sim$1200 ppm H_2 in the exhaust gas feed, while the high point corresponded to $\sim$2000 ppm. The volumetric flow of reformate produced at the two operating points were 3.2 dm^3/min and 3.9 dm^3/min, respectively. The temperature used for the low point was 800 °C meanwhile 850 °C was used in the high point. The H_2O/C ratio used in the PSR setup was higher, *cf.* the BSR setup, to enable a higher cleaning rate of the catalyst surface, since the catalyst could potentially be exposed to diesel in liquid state due to limitations in the diesel injection system.

The outlet concentrations of the fuel reformer used in the PSR setup oscillated due to limitations in the fuel and water injection apparatus. To compensate for these oscillations the collection time for NO_x reduction data was extended, ensuring statistically viable data.

3. Results

The NO_x reduction activity of three HC-SCR catalysts (Ag2, Ag4, Ag4Pt100) was initially investigated in a bench-scale reactor (BSR) setup, using a hydrogen-rich gas from a fuel reformer. Prior to these experiments the activity and durability of the fuel reformer catalyst (3 wt.% Rh/CeO$_2$-ZrO$_2$) was investigated, ensuring a reliable and stable supply of hydrogen. The HC-SCR catalyst that showed the largest promotional effect, as a function of hydrogen concentration, Ag4Pt100, was up-scaled and evaluated in a pilot-scale reactor setup (PSR). In the PSR setup the HC-SCR catalyst was exposed to

real operating conditions using real exhaust gases. The PSR setup enabled comparative experiments between hydrogen originating from bottle and from fuel reformer.

3.1. Hydrogen production over a 3 wt.% Rh/CeO$_2$-ZrO$_2$

Prior to the integration experiments the aging characteristics of the fuel reformer catalyst was thoroughly investigated. The investigation was performed in the bench-scale fuel reformer setup described in detail in ref. [28] with NExBTL. The most important feature for onboard fuel reforming in vehicle applications is the actual amount of hydrogen produced. In addition, the diesel slip *i.e.* the unconverted fuel passing through the reformer is of great importance, due to the fuel penalty as discussed previously. The concentration of hydrogen expressed in volume percent produced by the fuel reformer is seen in Fig. 3 as a function of time on stream. The concentration is based on dry reformate and compensated for dilution with inert gas. The diesel slip from the fuel reformer with time on stream is presented in Fig. 4. After 30 h on stream, the catalyst is stabilized resulting in an approximate concentration of 27 vol.% H_2 and a diesel slip of 7.5 vol.%. At lowered GHSV, after 65 h on stream, both an increase in H_2 selectivity and a decrease in diesel slip are observed, resulting in a H_2 concentration of approximately 30 vol.% and a diesel slip of 3 vol.%.

The main products in the reformate are H_2, CO_2, CO and H_2O, however the presence of by-products are not negligible. To have a better knowledge of the composition of the reformate, this was thoroughly investigated with an FT-IR gas analyzer, using the operating conditions utilized in the BSR experiments. The reformate
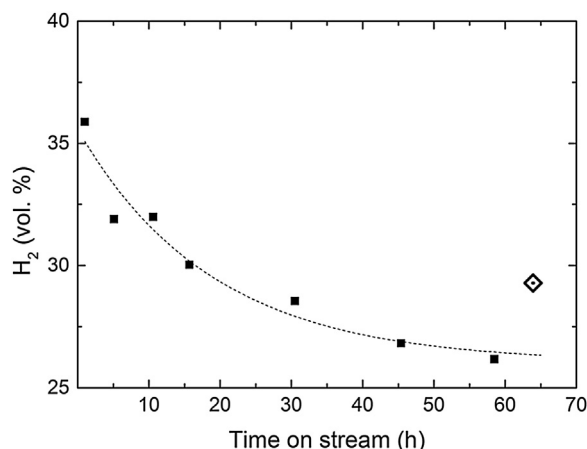
Fig. 3. Concentration of H_2 expressed in volume percent generated by the reforming catalyst as a function of time at 750 °C, O_2/C ~0.45 and H_2O/C ~2.5. The concentration is based on dry reformate and corrected for dilution. The GHSV is kept at ~50,000 h^{-1} in all points except the point after 65 h on stream ($\diamondsuit$) where the GHSV is decreased to ~20,000 h^{-1}.

composition is shown in Fig. 5, where the concentrations of the by-products are displayed as C_1-concentrations originating from each HC species.

During the BSR experiments the temperature in the fuel reformer was kept at relatively low temperature (750 °C), resulting in a high concentration of C_1 in the reformate originating from by-products. At elevated temperatures the contributions of C_1 from by-products is decreased. The actual C_1 concentration in the feed to the HC-SCR feed originating from by-products in the reformate depends on the volumetric flow of reformate, set to achieve the desired hydrogen concentration. A concentration of 2000 ppm C_1 in the reformate corresponds to a concentration of 10–40 ppm C_1 in the feed to the HC-SCR catalyst.

For the PSR experiments the composition of the reformate shown in Fig. 5 can only be seen as an approximate composition of the reformate. The main reason is the higher H_2O/C ratio used in the PSR experiments, causing a shift in mainly the CO/CO_2 ratio, due to the water-gas-shift reaction. In addition, the temperature is measured at different positions in the two fuel reformer reactors. Since the reformate composition is highly dependent on the temperature, this has to be accounted for. The temperature in the pilot-scale fuel
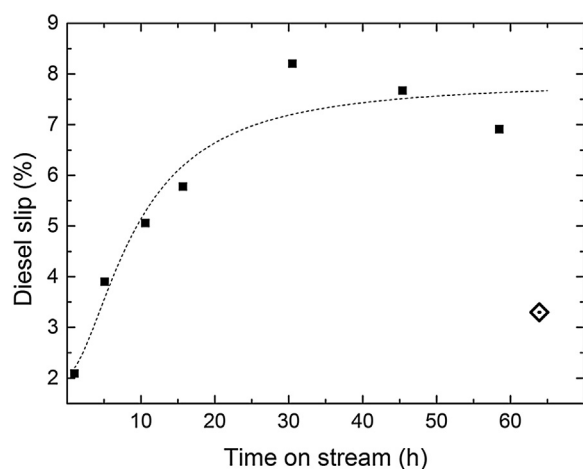

Fig. 4. Diesel concentration in the reformate with the fuel reformer running at 750 °C, O_2/C ~0.45 and H_2O/C ~2.5. The GHSV is kept at ~50,000 h^{-1} in all points except the point after 65 h on stream ($\diamondsuit$) where the GHSV is decreased to ~20,000 h^{-1}. Diesel slip is defined as the portion of diesel of total C_1 concentration in the reformate.
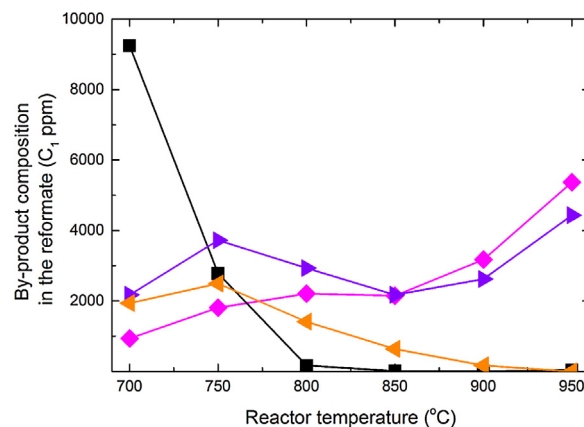

Fig. 5. Composition of the reformate at H_2O/C ~2.5 and O_2/C ~0.5 and GHSV ~20,000 h^{-1}. The concentrations of the by-products are displayed as C_1 derived from the different HC species. The species are denoted as: (■) diesel, (♦) CH_4, (◄) propene, and (►) ethene.

reformer corresponds roughly to a temperature 50 °C higher, *cf.* to the temperature during the BSR experiments in Fig. 5, *i.e.* 800 °C in the pilot-scale fuel reformer corresponds to an approximate reformate composition at 850 °C.

3.2. Thermal decomposition of NExBTL

A high activity over the HC-SCR catalyst is relying on an evenly distributed flow of reducing agent, *i.e.* fuel. If the fuel is exposed to high temperature the long hydrocarbon chains will decompose. The decomposition can be either cracking or partial and total oxidation. In the PSR, the reducing agent is injected through an air-assisted capillary, mounted right after the DOC. As stated before, the main purpose of the DOC is to heat the exhaust gas stream in order to have higher reaction temperatures in the HC-SCR catalyst. As a consequence, the reducing agent is normally exposed to temperatures higher than the reaction temperatures employed. To fully understand the thermal decomposition of NExBTL this was investigated in BSR experiments (Fig. 6).

In Fig. 6 the values are presented as percent of total C_1 for each HC species. One can see that NExBTL starts to thermally decompose slightly above 300 °C. At temperatures below 300 °C the majority of the hydrocarbons are present as diesel with just a fraction of CO and CO_2. The initial decomposition is followed by a sharp
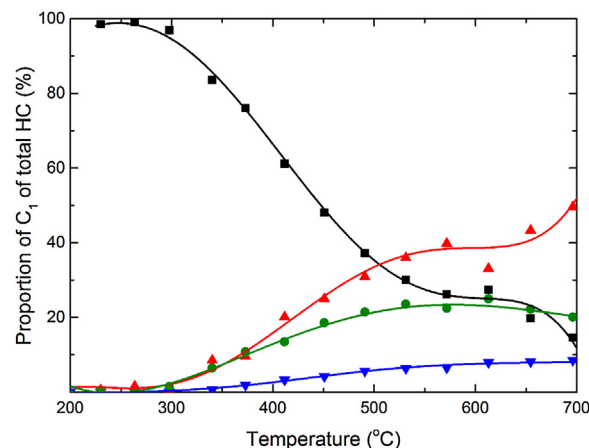

Fig. 6. Thermal decomposition of NExBTL in 10 vol.% O_2, 5 vol.% H_2O and N_2, balance. The species are denoted as: (■) diesel, (▲) CO_2, (▼) CO, and (●) propane.
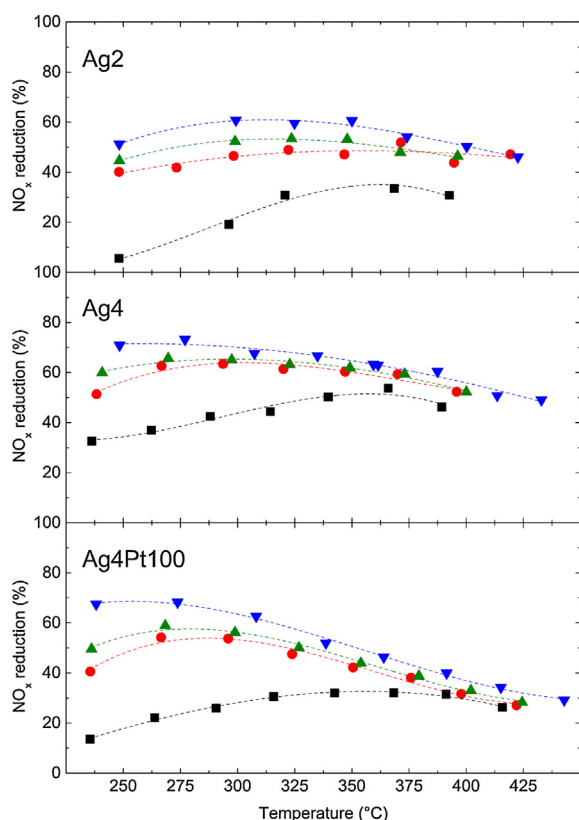
Fig. 7. NO_x reduction results from bench-scale reactor experiments for 2 wt.% (top panel), 4 wt.% (middle panel) and 4 wt.% with 100 ppm(w) Pt (bottom panel) Ag/Al_2O_3 samples. Hydrogen concentrations are denoted as 0 ppm (■), 1000 ppm (●), 1500 ppm (▲) and 3250 ppm (▼). Inlet gas composition: 200 ppm NO, 10 vol.% O_2, 5 vol.% H_2O, and $N_{2,balance}$ with NExBTL as reducing agent. The C/N molar ratio was 6 and GHSV = 33,200 h^{-1}.

Fig. 8. NO_x reduction results from pilot reactor experiments over a 4 wt.% Ag/Al_2O_3 catalyst doped with 100 ppm(w) Pt with bottled hydrogen (top panel) and hydrogen from a fuel reformer (bottom panel). Bottled hydrogen concentrations are denoted as ∼1400 ppm (●), ∼2800 ppm (▲), ∼7000 ppm (▼). Hydrogen was supplied from the fuel reformer at a low concentration (∼1200 ppm, ○) and a high concentration (∼2000 ppm, ◇). Inlet gas composition: ∼420 ppm NO_x, ∼10 vol.% O_2, ∼5 vol.% H_2O, $N_{2,balance}$ and NExBTL as reducing agent with a C/N molar ratio of ∼4 and GHSV ∼22,300 h^{-1}.

decrease in the diesel fraction and an increase in CO_2 and propane formation, followed by an increase in CO formation. This means that the dominating process, when treating NExBTL thermally, is complete oxidation with CO_2 and water as the main products. Propane seems to derive from a homogeneous cracking process. More surprisingly is that the CH_4, ethyne and ethane fractions remain negligible throughout the chosen temperature interval. Neither formaldehyde, nor propene or ethene are formed to a great extent, but remains around 2%. The temperature at the injection point of the reducing agent did in some cases reach 450 °C. This caused a decrease in the detected diesel signal, at the same time as the signals of the decomposition products increased. This corresponds well with the results from the thermal decomposition experiments. At 450 °C the contribution to total C_1 from diesel is as low as 45%, meanwhile CO_2 reaches almost 30% and propane is approximately 20%.

3.3. H_2-assisted lean NO_x reduction over Ag/Al_2O_3 in bench-scale

The NO_x reduction activity for three Ag/Al_2O_3 HC-SCR catalysts was evaluated using hydrogen supplied by a fuel reformer. The experiments were performed at four hydrogen concentrations 0, 1000, 1500 and 3250 ppm H_2 (Fig. 7). The fuel used in the fuel reformer and as reducing agent was commercial biodiesel (NExBTL). The promotional effect from adding hydrogen is clearly seen for all these catalysts. For example the NO_x reductions for the 0, 1000, 1500 and 3250 ppm H_2 are 33, 52, 61 and 72%, respectively, over the Ag4 sample at 225 °C. In addition, it can be observed that the effect of adding hydrogen is not proportional
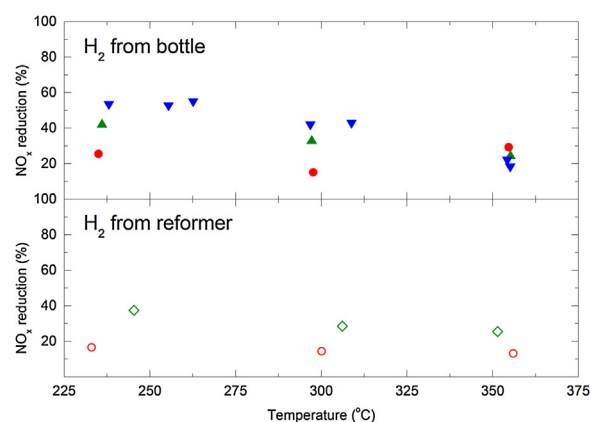
to the H_2 concentration. The improvement in NO_x reduction is most prominent at low temperatures and decreases as the temperature increases. The hydrogen effect can be seen over the entire temperature range for the Ag2 catalyst, whereas the effect is negligible for temperatures above 400 °C for both the Ag4 and Ag4Pt100 catalysts (Fig. 7). This is likely due to the increased amount of oxidation sites for these two catalysts, oxidizing the majority of the H_2 to H_2O at higher temperatures. The catalyst showing the lowest effect of H_2 for reduction of NO_x at higher temperatures is the platinum doped one. Platinum is a well-known oxidation catalyst and at higher temperatures it is likely to oxidize the H_2 rather than use it in the NO_x reduction reactions [16]. On the contrary, the largest difference in low-temperature activity when adding hydrogen is seen for the Ag4Pt100 catalyst. When hydrogen is added the NO_x conversion increases from 13% to 68% with an addition of 3250 ppm H_2. This catalyst also shows the most distinct change in activity with increasing H_2 concentrations. Furthermore, it can be seen that the concentration dependence of H_2 on the NO_x conversion is lower for the Ag2 sample *cf.* to the Ag4 and Ag4Pt100 samples. When hydrogen from reformate was used a clear exotherm over the HC-SCR catalyst was observed (Fig. 7) as the data points are shifted to higher temperatures with increasing H_2 concentration. The exotherm also increased with silver loading and platinum doping in the following order: Ag2 < Ag4 < Ag4Pt100.

3.4. H_2-assisted lean NO_x reduction over Ag/Al_2O_3 in pilot-scale

To expand the integration experiments to more realistic operating conditions, the HC-SCR catalyst was evaluated using an engine (genset, DX 6000 TE XL C, Yanmar) and a separate fuel reformer for hydrogen production. The fuel used in the reformer and as reducing agent was commercial biodiesel (NExBTL). The HC-SCR catalyst chosen for PSR experiments was the 4 wt.% Ag/Al_2O_3 sample doped with 100 ppm(w) Pt (Ag4Pt100), displaying the largest hydrogen promotional effect. It also shows the most distinct variations in the activity for NO_x reduction as a function of the amount of added hydrogen at low temperatures. The Ag4Pt100 HC-SCR catalyst was evaluated, using both bottled hydrogen (Fig. 8, top panel) and hydrogen from the fuel reformer (Fig. 8, bottom panel). The bottled hydrogen was introduced at three concentrations (∼1400, ∼2800 and ∼7000 ppm), resulting in a NO_x reduction of 25, 42 and 53% at ∼236 °C, respectively, and the hydrogen from the fuel reformer

was introduced at two concentrations: one low (~1200 ppm) and one high (~2000 ppm) resulting in a NO_x reduction of 16% at 233 °C and 37% at 245 °C, respectively. The NO_x reduction was calculated by analyzing the total NO_x concentration both upstream and downstream of the HC-SCR catalyst with an FTIR gas analyzer. The C/N ratio was lowered to approximately 4 for these experiments, in order to reduce the adsorption of diesel residues on the HC-SCR catalyst. At higher C/N ratios, a slow decrease in NO_x reduction could be monitored over time. When the reducing agent was removed, a decreasing CO and diesel signal could be detected for as long as 15 min. This indicated that carbonate species were adsorbed on the catalytic surface, possibly blocking the active sites, which also has been observed previously [26]. Hence, no reliable data could be collected without hydrogen present in the feed.

The temperature measurement of the reaction temperature was, due to the reactor design, measured approximately 25 cm upstream of the HC-SCR catalyst brick and no temperature measurement could be performed downstream of the HC-SCR catalyst brick. In addition, the ability to insulate the HC-SCR module was limited, resulting in an overestimation of the catalyst temperature of no less than 50 °C. In order to compensate for this, the NO_x reduction in Fig. 8 is plotted against an estimated temperature, 50 °C below the measured temperature, however this temperature may as well be overestimated. The results from the PSR study show similar trends as the BSR experiments. The NO_x reduction activity is significantly increased with addition of bottled hydrogen at low temperatures and as the temperature is increased the promotional effect is less pronounced (Fig. 8) with no statistical difference above 350 °C. As no data are available for conditions without hydrogen, the actual promotional effect cannot be determined. However, when adding 1400 ppm H_2 cf. to 7000 ppm H_2 from bottle, the reduction can be seen to double with an increase from 25% to 53%. When using hydrogen produced in the fuel reformer, the same trend can be observed.

4. Discussion

As stated previously the promotional effect of hydrogen for lean NO_x reduction over Ag-alumina catalysts has been studied extensively since it was first discovered in 2000 [11]. Many suggestions as to the reaction mechanisms have been proposed, and still the scientific community has not reached an overall consensus. This study does, however, not aim to explain the chemistry behind the phenomenon but instead wishes to illustrate the difference on the effects when using bottled hydrogen cf. hydrogen produced in a fuel reformer. The latter has been proposed as the most viable option for hydrogen-based technologies in truck applications. The major part of the produced hydrogen would be utilized in an auxiliary power unit (APU), producing electricity during standstills and thereby reducing the total amount of anthropogenic CO_2 emissions.

To reach a high NO_x reduction activity at low temperatures in the pilot-scale reactor setup, a relatively high concentration of hydrogen is needed. When the temperature is increased, the concentration of hydrogen becomes less crucial for the NO_x reduction efficiency. As the demand for hydrogen depends on the temperature in the HC-SCR catalyst it is important to have a hydrogen supply which is easy to regulate. Therefore, a separate fuel reformer is preferred over conversion of the EGR gases with additional fuel injection. Such a system cannot be regulated separately from the engine mode and the hydrogen production will therefore be closely coupled to the engine operation. A separate fuel reformer, on the other hand, can be regulated independently of the engine and the hydrogen production can be adapted to the needs of the HC-SCR catalyst. The main benefit of installing a separate fuel reformer is however the possibility to decrease emissions and fuel

consumption during idling by generating electricity in an APU, compensating for parts of the fuel penalty arising from the use of HC-SCR.

This study progressed from initially evaluating and optimizing the reformer catalyst and the HC-SCR catalyst separately [14,28]. The reformer catalyst was aged in order to receive a stable reforming of fuel to hydrogen, ensuring a reliable hydrogen supply. The integrated system of fuel reformer and HC-SCR catalyst was then investigated in a controlled environment in an integrated bench-scale reactor setup, ensuring the compatibility of the two systems. In addition, the HC-SCR catalyst displaying the largest variation in the promotional effect from hydrogen (Ag4Pt100) was chosen for the PSR experiments. A scaled up cordierite brick (1.2 dm^3) was coated and used to reduce NO_x from real engine exhaust gases with hydrogen supplied both from bottle and from a separate fuel reformer. From the ageing experiments of the reformer catalyst, a fast initial deactivation could be observed, decreasing the hydrogen outlet concentration and increasing the diesel slip. This fast initial deactivation is most likely due to sintering of Rh particles, resulting in decrease of active sites. The deactivation does, however, level out and after more than 70 h the hydrogen concentration can be assumed to be constant around 30 vol.% at GHSV ~20,000 h^{-1}. The outlet concentration from the fuel reformer was however monitored regularly in both reactor setups, ensuring that the hydrogen feed to the HC-SCR system was correct.

The NO_x reduction results from the BSR shows a very large promotional effect from reformate. Both the Ag4 and Ag4Pt100 samples displayed NO_x reductions of about 70% below 300 °C, with Ag4Pt100 displaying the largest variation in activity as a function of hydrogen concentration. The highest promotional effect in NO_x reduction activity, owing to the addition of hydrogen, is observed at low temperatures and the effect decreases with increasing temperature. This is likely due to oxidation of hydrogen to water at higher temperatures [26]. Compared to previous studies [30] the low-temperature NO_x reduction in BSR experiments displayed a higher activity using reformate cf. bottled hydrogen [30]. This increase most likely originated from HC species in the reformate. The main components in the reformate are H_2, H_2O, CO and CO_2, however other carbon-containing species are present e.g. propene and other short chain HC (Fig. 5). For simplicity the concentrations in Fig. 5 is calculated as C_1 concentration. The two major contributors to the C_1 concentration are propene and ethene. Hence, the C_1 concentration in the synthetic exhaust gas in the BSR setup is increased with 40–150 ppm, depending on the current hydrogen concentration. Increasing the concentration of C_1 in the feed will improve the NO_x reduction activity, effectively increasing the C/N ratio. As a large portion of the additional HC present is propene, this will also likely result in an additional improvement as propene (Fig. 5) and propane (Fig. 6) have proven to be among the strongest reducing agents for HC-SCR [11]. Another contributing property is unsaturation where higher unsaturation gives a stronger reducing agent [31]. In the bench-scale reactor experiments an exotherm is generated over the HC-SCR catalyst when introducing hydrogen from the fuel reformer. This can be compared to the negligible exotherm when using bottled hydrogen in BSR experiments (not shown). Consequently, the exotherm when using reformate hydrogen is assumed to derive from the reformate itself, most likely owing to oxidation of various carbon-containing species. An increased exotherm is observed with increased reformate feed. In addition the exotherm is larger for samples with higher silver loading and higher still for the catalyst doped with platinum. This is likely an effect of an increase in the number of Ag oxidation sites as well as a slight increase in the oxidation potential from the platinum [14].

As stated above, the catalyst (Ag4Pt100) showing the largest variation in the promotional effect of reformate addition in the

BSR experiments was scaled up and evaluated in the pilot-scale reactor setup. The PSR gives a unique opportunity to evaluate the HC-SCR catalyst in real exhaust gases. The reactor setup also enables a comparative evaluation between bottled hydrogen and hydrogen supplied from a fuel reformer. The maximum NO_x reduction activity of up to 55% was achieved using bottled hydrogen (7000 ppm H_2) at temperatures below 325 °C. When using hydrogen from the fuel reformer, approximately 28% NO_x reduction is reached with 2000 ppm H_2 around 300 °C *cf.* approximately 32% NO_x reduction with 2800 ppm H_2 from bottle, illustrating the beneficial effect of reformate as compared to bottled hydrogen.

When the reducing agent is introduced at a C/N ratio of 6, a decrease in NO_x reduction could be observed over time. When dosing of the reducing agent is terminated, decreasing CO and diesel signals can be detected, downstream of the HC-SCR catalyst, for as long as 20 min. This indicates a poisoning of the active sites, likely due to HC condensation and adsorption on the surface. The adsorbed HC species may be due to locally higher concentration of NExBTL as a consequence of an uneven flow pattern in the PSR setup. After the injection point of the reducing agent, the gas-flow is redirected through two 90° bends before reaching the HC-SCR catalyst, thus wall effects and other contributions may have influenced the flow distribution of the reducing agent. Hence, the C/N ratio in the PSR experiments is decreased to approximately 4, in order to avoid diesel build-up on the catalyst surface. Additionally, the injection point for the reducing agent is located close to the DOC, at relatively high temperatures (approx. 450 °C) due to diesel oxidation reactions, likely resulting in a decomposition of the reducing agent. At 450 °C more than 40% of the injected NExBTL (based on C_1 concentration) is present as CO_2 and CO. It has been shown that CO, CH_4 and CO_2 do not contribute to the NO_x reduction activity over Ag/alumina catalysts [20]. It has been shown that CO, CH_4 and CO_2 do not contribute to the NO_x reduction activity over Ag/alumina catalysts [20]. This likely contributes significantly to the lowering of the conversion for the PSR results *cf.* to the BSR results.

5. Conclusions

This study illustrates the importance of evaluating HC-SCR catalysts in combination with a fuel reformer at real conditions, due to the effects of the reformate. It further illustrates that adding hydrogen-rich gas from a fuel reformer results in a higher NO_x reduction *cf.* to the same amount of hydrogen from bottle, seen in both bench scale experiments and pilot scale experiments. The increase in NO_x reduction activity is likely owing to the reactive HC species in the reformate in combination with the hydrogen.

The highest low-temperature activity during the bench-scale experiments can be observed for the Ag4 and Ag4Pt100 samples (~70% below 300 °C with 3250 ppm H_2 from reformate). It is worth noted that 40% NO_x reduction was achieved with 2000 ppm H_2 originating from the fuel reformer *cf.* to 2800 ppm H_2 needed from bottle to reach the same NO_x reduction. The largest difference in the promotional effects, as a function of reformate concentration, can be seen for the Ag4Pt100 sample. At real engine exhaust conditions the Ag4Pt100 catalyst showed a NO_x reduction of ~60% in the pilot-scale reactor setup with 7000 ppm H_2 (bottle) at 275–300 °C. It can also be noted that the temperature in the reducing agent injection zone is crucial. This is due to possible decomposition of the hydrocarbons, to non-active carbon species *e.g.* CO, CO_2, and CH_4 at elevated temperatures.

The research gives a unique approach to an improved understanding of the total hydrogen assisted lean NO_x reduction system. This study covers the development of catalytic materials evaluated in controlled bench-scale experiments, followed by integrated bench-scale experiments of the lean NO_x and fuel reformer to a final evaluation of the integrated system in an engine bench reactor setup. Therefore, our study proves a viable concept for lean NO_x reduction together with onboard hydrogen production.

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